



TiO_{2-x}/CoO_x photocatalyst sparkles in photothermocatalytic reduction of CO₂ with H₂O steam

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ABSTRACT

Solar photocatalytic production of fuels from CO₂ and H₂O remains a challenging goal. Herein we report a strategy to co-modify TiO₂ with oxygen vacancies and CoO_x nanoclusters for enhanced photothermocatalytic reduction of CO₂. The TiO_{2-x}/CoO_x material exhibits prominently enhanced activity for the yield of CH₄ and CO under ultraviolet irradiation at elevated temperature of 393 K, which is 111.3- and 13.2-times greater yield of CH₄ and CO, respectively than the conventional photocatalytic process at 298 K, and 175.1- and 2.9-times greater yield of CH₄ and CO, respectively than the pristine TiO₂ under the same photothermocatalytic conditions. Control experiments over singly modified TiO₂ and doubly modified TiO₂ by different preparation history, together with high-resolution transmission electron microscope (HRTEM), electron spin resonance (ESR), and transient photovoltage measurements reveal the synergistic effect of oxygen vacancies and surface-grafted CoO_x on the photothermocatalytic reduction of CO₂ to CH₄, i.e. oxygen vacancies at TiO₂ surface facilitate the adsorption and reduction of CO₂ and the dispersion of CoO_x nanoclusters, whereas surface-grafted CoO_x clusters facilitate the hole trapping and the oxidation of H₂O. Thereby the coexistence of oxygen vacancies and CoO_x nanoclusters at TiO₂ surface promote the separation of photogenerated electrons and holes, and remarkably enhance the eight-electron reduction of CO₂ to CH₄ under photothermocatalytic conditions. This study shows the great potential of photo-thermal synergy on CO₂ reduction and provides a promising means to design photothermocatalysts for solar photocatalytic reduction of CO₂ to fuel.

1. Introduction

Artificial photosynthesis, which involves water splitting and CO₂ reduction processes inspired by natural photosynthesis, has attracted increasing interest for sustainable fuel production [1–4]. However, artificial photosynthesis by the above two processes is still challenged by low conversion efficiency and low selectivity of products [5–7]. Recent research has shown great promise of photo-thermal synergy for the catalytic reduction of CO₂, by which a catalyst can exhibit activity for CO₂ reduction far exceeding the sum of photocatalytic activity and thermocatalytic activity in a photothermocatalytic process [8–12]. From a viewpoint of chemical thermodynamics [13], coupling photo-excitation with heating can favor the artificial photosynthesis by the following advantages: (1) heating helps the CO₂ reduction proceed because of an endothermic reaction; (2) heating water above 373 K converts liquid to gas whereby gaseous H₂O and CO₂ are uniformly mixed, overcoming the normally low solubility of CO₂ in H₂O; and (3) heating particularly accelerates the rate of reaction with a larger

activation energy according to Arrhenius equation, i.e. the water oxidation reaction in the case of artificial photosynthesis [14]. In these regards, it is in urgent demand to develop photothermocatalysts to tackle the low conversion efficiency and low selectivity issues of artificial photosynthesis.

Inorganic semiconducting materials are workhorse for photocatalytic reduction of CO₂ with H₂O, of which conversion efficiency and selectivity are dependent on the capability of light absorption, charge separation and charge transfer pathways at the surface [15–18]. The semiconducting photocatalyst is often loaded with nanosized co-catalysts to enhance charge separation and modulate the reaction pathways of CO₂ reduction and water oxidation [19–22]. A number of studies focus on noble metal cocatalyst to promote CO₂ reduction reaction via electron transfer [23–25]. However, under the premise of CO₂ reduction with H₂O, the hole transfer is no less important than electron transfer [20,26]. MO_x (M = transition metal) nanoclusters are also frequently employed as co-catalysts either for electron or hole transfer dependent on composition [27–31]. Yamakata et al. studied the

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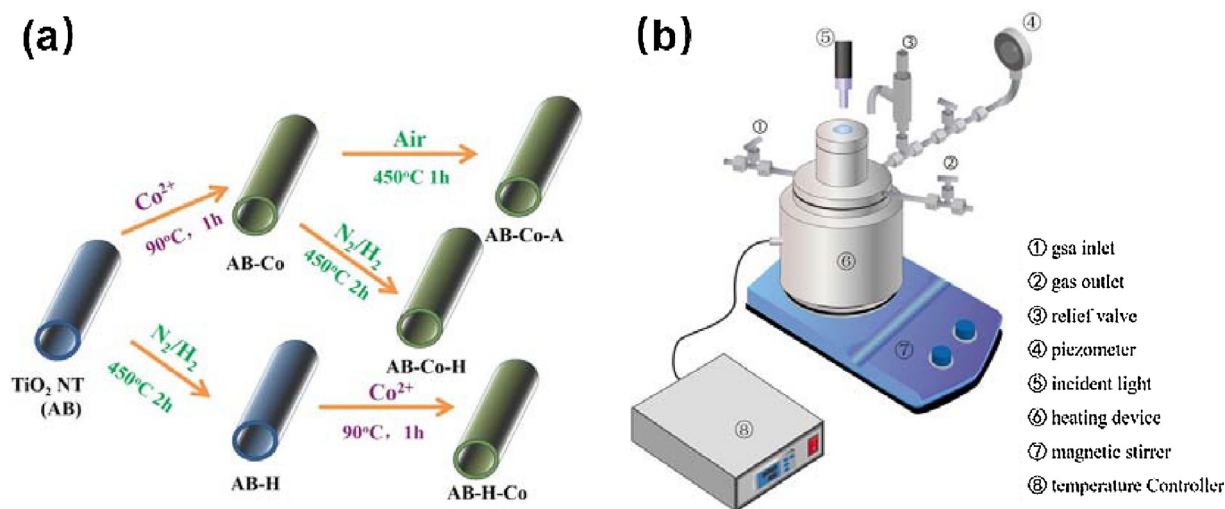
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Scheme 1. (a): The synthetic process of catalysts; (b): Schematic diagram of reaction device.

behavior of photogenerated charge carriers over $\text{CoO}_x/\text{LaTiO}_2\text{N}$ by time-resolved visible to mid-infrared absorption and compared with that of $\text{Pt}/\text{LaTiO}_2\text{N}$ [32]. They observed that holes were captured rapidly by CoO_x in a few picoseconds and whereas electrons transfer by Pt proceeded over 0–100 μs , demonstrating the better role of CoO_x cocatalysts for hole transfer. In fact, many reports have described effective CoO_x cocatalyst for boosting water oxidation, including BiVO_4 , TaON , WO_3 , and TiO_2 supports [19,33–36]. Thus, CoO_x cocatalyst deserves further investigation on CO_2 reduction with H_2O . In particular, photo-thermocatalysis process is more complicated than that of photocatalysis, and additional photo-thermal synergy should be considered and closely correlated with behaviors of charge carriers over CoO_x cocatalyst.

Another tough issue about artificial photosynthesis is the activation of CO_2 [37]. Recent study by Dong et al. [38] highlights that cocatalyst shows a prominent size effect for both activity and selectivity in CO_2 reduction. They revealed that smaller Pt nanoparticles showed superior performance in both CO_2 reduction and H_2 evolution because of promoted charge transfer efficiency; and whereas larger Pt nanoparticles showed a higher CH_4 selectivity because of higher proportion of surface terrace sites. On the other hand, recent theoretical calculations and experiments have proven that the introduction of oxygen vacancies onto TiO_2 decreases the energy of CO_2 adsorption and activation [39,40]. Further, the oxygen vacancies tend to strongly interact with surface-grafted MO_x clusters [30,40,41]. This ensures ultra-dispersion of surface MO_x cocatalyst and decreasing the size of cocatalyst. Thus, it is expected that a combination or even the synergy of oxygen vacancy and surface MO_x cocatalyst can efficiently activate the TiO_2 for photo-thermocatalytic reduction of CO_2 . Herein, we propose a strategy that combines hydrogen treatment and CoCl_2 impregnation to co-modify the TiO_2 support. The anatase/ $\text{TiO}_2(\text{B})$ nanotube was selected as support because of its high surface area for ultra-dispersion of cocatalyst. This promotes charge separation at the interface of anatase/ $\text{TiO}_2(\text{B})$ [42]. CoO_x nanoparticles were formed by hydrolysis of CoCl_2 on the surface of TiO_2 and their size could be varied by varying modification process. Structural characterization reveals that a $\text{TiO}_{2-x}/\text{CoO}_x$ catalyst is achieved in which CoO_x nanoparticles with a diameter below 2 nm offer a surprising activity for CH_4 production. This yield can be 175 times higher than that of pristine TiO_2 , which indeed confirms a significant photothermal synergy. The reasons for the high activity of $\text{TiO}_{2-x}/\text{CoO}_x$ photo-thermocatalyst are systematically understood via capture of CO_2 at oxygen vacancy, dual charge separation by oxygen vacancy and CoO_x cocatalyst, and multiple electron/proton accumulation at the interface of $\text{TiO}_{2-x}/\text{CoO}_x$.

2. Experimental section

2.1. Synthesis of samples

The synthesis of TiO_2 and CoO_x modified TiO_2 : TiO_2 support was synthesized by a method reported previously [42]. The nanotubes composed of anatase and $\text{TiO}_2(\text{B})$ were obtained by calcination at 450°C for 2 h. For simplicity, TiO_2 sample with anatase and $\text{TiO}_2(\text{B})$ was named AB. A simple impregnation was employed to graft CoO_x nanoparticles on $\text{TiO}_2(\text{AB})$ nanotubes. The 0.5 g $\text{TiO}_2(\text{AB})$ was dispersed in 10 ml of deionized water, followed by 5 mL of CoCl_2 ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Tianjin guangfu technology development Co. Ltd., 99.0%) solution (2.04 mM) to the suspension. The suspension was further stirred at 90°C for 1 h. Finally, the as-obtained light green powders were centrifuged, washed with water, and dried at 110°C for 24 h. For simplicity, this sample was named AB-Co. For comparison, AB-Co was calcined in air at 450°C for 2 h and named AB-Co-A.

Synthesis of defective TiO_2 and grafting CoO_x on defective TiO_2 : To introduce oxygen defects into TiO_2 , the AB sample was calcined at 450°C for 2 h in $\text{N}_2/\text{H}_2(9:1)$ mixture with a flow speed at 125 mL/min in the tube furnace, which is named AB-H.

The order of hydrogenation and CoO_x grafting was considered when oxygen defects and CoO_x were simultaneously integrated on TiO_2 . The two samples were named AB-H-Co and AB-Co-H. Here, AB-H-Co means AB sample modified by hydrogenation followed by CoO_x grafting and AB-Co-H means AB sample modified by CoO_x grafting, followed by hydrogenation. Scheme 1a illustrates the synthesis route of all samples.

Details about the characterization are described in the supporting information.

2.2. Photothermal reduction of CO_2

Photothermal reduction of CO_2 used an autoclave (Anhui Kemi Machinery Technology Co., Ltd.) with a total volume of 100 ml. First, 0.05 g catalyst powders and 2 mL of deionized water were added to the autoclave. Then, the reactor was blown with CO_2 (99.999%) for 20 min to ensure that the reaction system was filled with pure carbon dioxide. Finally, the clave was sealed, heated to 393 K irradiated from the top with a 150 W UV lamp (Hayashi UV410). Scheme 1b illustrates the reaction device. The window area for light irradiation was 3 cm^2 , and the circular groove area for powder catalyst was 13.9 cm^2 , respectively. The light intensity irradiated on the samples was $20\text{ mW}/\text{cm}^2$ at 365 nm. The generation of CO and CH_4 was monitored using a gas chromatograph (model GC-2014, Shimadzu Co., Ltd.). For comparison, a photocatalytic test was performed at room temperature and other

conditions remained the same as the photothermocatalytic test.

3. Results and discussion

We prepared anatase/TiO₂(B) nanotubes (named AB) as reported in our previous work [42]. The lattice mismatch at the interface of anatase (101)/TiO₂(B) (110) is 1.36% [43,44], which is much lower than the 7.76% mismatch at the anatase (101)/rutile (110) interface, suggesting a better suppression of charge recombination of anatase/TiO₂(B) than anatase/rutile. Moreover, one dimensional AB nanotubes provide a better charge transport. The surface area of as-adopted AB nanotubes is as high as 277 m² g⁻¹, which not only benefits the ultra-dispersion of CoO_x cocatalyst, but it also offers many active sites for the catalytic conversion of CO₂.

Photothermocatalysis is more complicated than photocatalysis and the synergy of photocatalysis and thermocatalysis should be considered. The well-known mechanisms in photocatalysis might not be applied to photothermocatalysis. In photocatalysis, the introduction of oxygen defects into the photocatalyst effectively boost the activity until a significant visible absorption of TiO₂ is observed [45]. In another word, slight oxygen defects lead to insignificant visible absorption that does not improve the photocatalytic activity. It is not clear if an inactive photocatalyst with slight oxygen defect leads to an inactive photothermocatalyst. On the other hand, the loading amount of MO_x cocatalyst onto TiO₂ photocatalyst is usually 1–10 wt%. When the loading amount of cocatalyst is lower than 1 wt%, it is difficult to observe any activity enhancement. Thus, we wonder whether a photocatalyst with a cocatalyst lower than 1 wt% implies an inactive photothermocatalyst.

To address these gaps in knowledge, we intentionally introduced a slight oxygen vacancy and ultra-low amount of CoO_x cocatalyst onto AB nanotubes. In photocatalysis, neither the introduction of slight oxygen vacancy nor the ultra-low amount of CoO_x cocatalyst significantly enhances the photocatalytic activity. In spite of the slight modification, the strategy can significantly activate TiO₂ in photothermocatalysis. To clarify the superior performance of TiO_{2-x}/CoO_x in photothermocatalysis versus photocatalysis, we next focus on six typical samples of AB, AB-H, AB-Co, AB-Co-A, AB-Co-H, and AB-H-Co to demonstrate the contribution of each modification. By systematic comparison, the single role of oxygen vacancy, CoO_x cocatalyst, as well as the synergy effect between oxygen vacancy and CoO_x cocatalyst on the photothermocatalytic activity are studied.

3.1. Ultra-dispersion of CoO_x nanoparticles on AB nanotubes and further decrease of size on AB-H nanotubes

The morphological structures of samples were observed by SEM and TEM. As shown in Fig. 1a, AB sample takes on one-dimensional nanostructure feature. From the TEM pictures (Fig. 1b), it can be characterized nanotubes with a diameter of ca. 10 nm. There is no appreciable morphological change regardless of thermal treatment in air or N₂/H₂ (Fig. S1–S2), indicating that AB nanotubes have a good thermal stability. In addition to the above AB and AB-H nanotubes, grafting CoO_x species on AB nanotubes was performed under three cases. After grafting, the measured atomic percentage of Co in AB-Co-H, AB-Co, and AB-H-Co was 0.19 wt%, 0.19 wt% and 0.15 wt% indicated by ICP element analysis respectively, which is in accordance with the starting stoichiometric ratio (0.12 wt%) in the synthesis process. Theoretically, 0.12 wt% Co grafting corresponds to 0.046 Co atom per nm² by assuming that CoO_x species are uniformly distributed on the surface of AB nanotube. Thus, the grafted CoO_x species onto TiO₂ are supposed to be highly separated from each other and are ultra-small [46].

The HAADF image of the as-obtained AB-Co-H sample is acquired and shown in Fig. 1c. Bright nanoparticles are uniformly distributed around the dark nanotubes, confirming that CoO_x nanoparticles were successfully grafted on the defective AB nanotubes. The HRTEM image (Fig. 1g) shows that the diameter of CoO_x nanoparticles is ca. 5 nm. The

FFT pattern indicates that CoO_x nanoparticles are crystallized into CoO nanocrystals, as shown in Fig. S3. FFT pattern of shedding nanoparticles from sample AB-Co-H is of hexagon shape. The spots and angles between spots can be well assigned to CoO along [124] zone axis. Element mapping was further conducted to determine the distribution of component elements. As can be seen and compared in Fig. 1d–f, elemental Co was uniformly distributed on the nanotubes. When AB nanotubes were only modified by CoO_x nanoparticles, HRTEM image of AB-Co sample gives a diameter of CoO_x nanoparticles ca. 2 nm, as shown in Fig. 1h. FFT pattern suggest that the CoO_x nanoparticles are amorphous. The smaller diameter compared with that of AB-Co-H is believed to result from the aggregation of CoO_x nanoparticles by the thermal treatment during hydrogenation of AB nanotubes. When the CoO_x nanoparticles were grafted onto AB-H nanotubes, they are too small to be observed by HRTEM, as shown in Fig. 1i. The smallest CoO_x nanoparticles among three CoO_x grafted TiO₂ samples may benefit from strong interactions between oxygen vacancy defects and CoO_x nanocluster, which will be discussed in detail via other characterization. Accordingly, it can be concluded that CoO_x nanoparticles can be ultradispersed on AB nanotubes. The size of CoO_x nanoparticles in these three samples ranges in the following order: AB-Co-H > AB-Co > AB-H-Co. The CoO_x nanoparticles on AB-Co and AB-H-Co are amorphous whereas the CoO_x nanoparticles on AB-Co-H are crystallized into CoO nanocrystals.

3.2. Phase composition

X-ray diffraction (XRD) characterization was performed on the Si substrate to calibrate the position of the diffraction peaks of TiO₂ sample. After calibration, the diffraction pattern of AB (Fig. 2a) can be identified as mixed phases of anatase (JCPDS file no.21-1272) and TiO₂(B) (JCPDS file no.46-1237). The modifications, including hydrogenation and CoO_x grafting, lead to no change of original diffraction pattern, due to the slight oxygen vacancy and ultra-low amount of CoO_x. Raman spectra (Fig. 2b) can provide further information on the phase composition and defects in TiO₂. As shown in Fig. 2b, the bands at 144, 197, 399, 515, and 639 cm⁻¹ are corresponding to E_g, E_g, B_{1g}, A_{1g} + B_{1g}, and E_g modes of anatase [47]. The bands at 119.5 cm⁻¹ and 251.4 cm⁻¹ are assigned as TiO₂(B) [48]. On close inspection of the E_g band at 144 cm⁻¹ in AB-H and AB (Fig. 2c), we note a subtle shift to higher wavenumber after hydrogenation of AB nanotubes, which indicates the existence of structural disorders related to the oxygen vacancies in AB-H sample [49,50].

(c) Magnified Raman spectra of AB and AB-H in the regions of 133–155 cm⁻¹.

3.3. Analysis on local environment around grafted CoO_x species

Fig. 3a displays the UV–vis spectra of different samples. In the region between 200 and 500 nm, CoO_x grafting hardly change the absorption of AB nanotubes, which agrees with the ultra-low amount of CoO_x nanoparticles. Meanwhile, hydrogenation results in only minor visible light absorption, indicating that a slight oxygen vacancy was introduced. There is also an absorption peak at 550–670 nm in the CoO_x modified TiO₂ sample. As reported, d-d electron transition of Co²⁺ gives a very similar absorption in the same region [51]. On recalling the aforementioned results of HRTEM image of AB-Co-H, the CoO_x nanoparticles existed in terms of CoO crystal. Therefore, it is believed that the additional absorption at 550–670 nm in AB-Co-H originates from the d-d electron transition of octahedral Co²⁺. Since there is no obvious difference between the d-d electron transition-related absorption in all CoO_x modified samples, it is deduced that the as-grafted CoO_x species in all samples exist in the state of Co²⁺.

The bonding environment of elements in different samples is further analyzed by XPS. Note that no Co related XPS peaks appear over all CoO_x modified samples (Fig. S5). This is because the amount of grafted

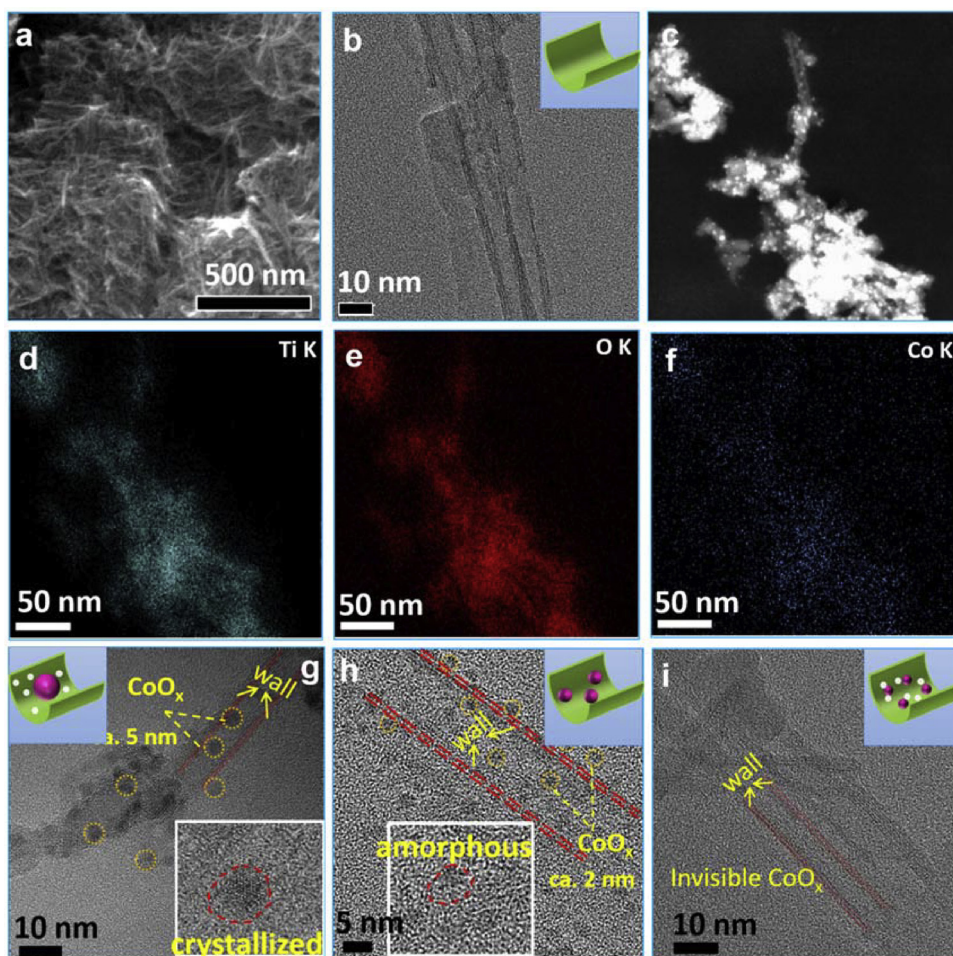


Fig. 1. (a) SEM image of AB; (b) TEM image of AB; (c) HAADF images and (d–f) EDS mappings of AB-H-Co; (g–i) HRTEM images of AB-Co-H, AB-Co, and AB-H-Co; insets are the models of the samples.

CoO_x (0.15–0.19 wt%) is far lower than the detection limit of 0.6 wt% for Co element according to the precision of the instrument. Figs. 3b and 3c show the XPS peaks of Ti 2p and O 1s of all samples. For AB sample, there are two individual peaks at 458.47 eV and 464.17 eV, which can be indexed to Ti 2p_{3/2} and Ti 2p_{1/2} binding energy of Ti⁴⁺ state [52,53]. For samples AB-Co and AB-Co-A, the binding energy of the Ti 2p peaks exhibit a slight shift to higher value. This is related to the formation of Ti–O–Co bond via the surface bonding between Co and Ti, due to the higher electronegativity of Co than that of Ti [54–56]. In contrast, for AB-H sample, the peaks of Ti 2p and O 1s

slightly shift to lower BE, which is related to the introduction of oxygen vacancy defects via hydrogen treatment [57]. Samples AB-Co-H and AB-H-Co have little shift in the binding energy of Ti 2p and O 1s likely because of a synergistic effect between the oxygen vacancy and the CoO_x grafting. However, it is noted that the peak of Ti 2p in AB-H-Co shifts to higher binding energy. In fact, as observed in the HRTEM images, CoO_x on AB-H-Co has a higher dispersion and smaller size than that on AB-Co-H. This indicates a stronger interaction between CoO_x and TiO₂ in sample AB-H-Co. In view of positive shift of Ti 2p peak induced by CoO_x grafting, it is believed that higher binding energy of

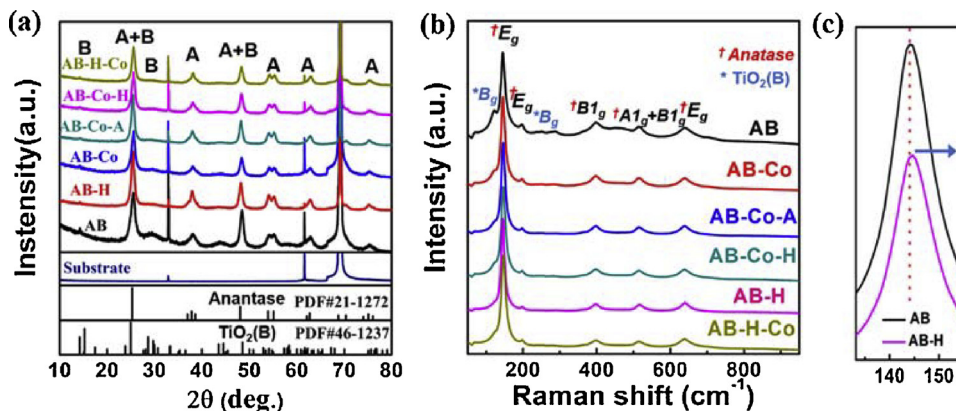


Fig. 2. (a) XRD patterns of different samples, (b) Raman spectra of different samples.

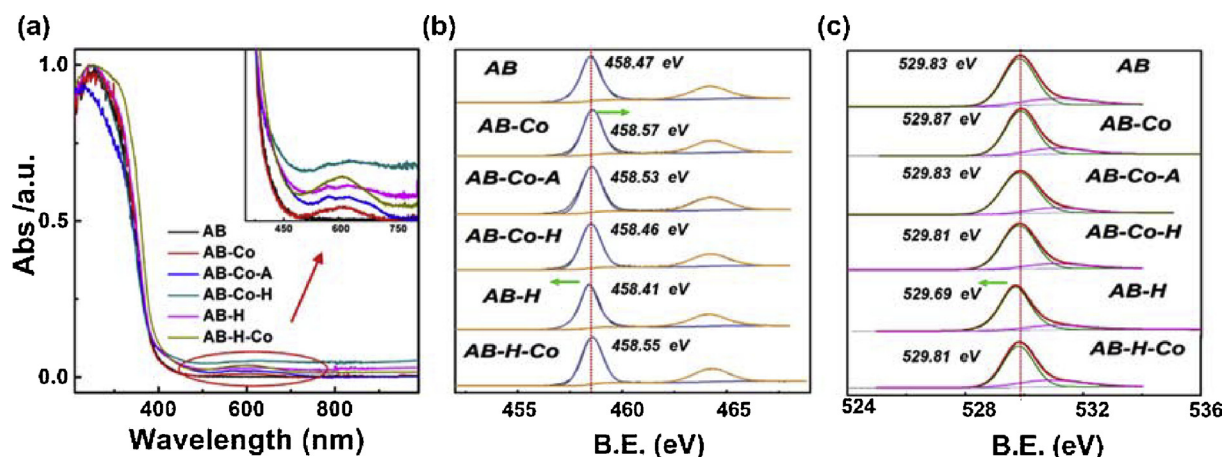


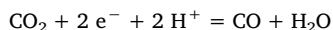
Fig. 3. (a) UV-vis spectra of different samples; (b) XPS spectra of Ti 2p and (c) O 1s core level of the as-prepared samples; all peak maxima were calibrated to C1 s at 284.6 eV.

Ti2p peak in AB-H-Co than AB-Co-H results from a better dispersion of CoO_x and stronger interaction between CoO_x and TiO_2 .

3.4. The photothermal synergy in CO_2 reduction over AB-H-Co

Fig. 4 shows the results of catalytic reduction of CO_2 over sample AB-H-Co. By photocatalysis, the production rate of CO and CH_4 is 1.2473 and 0.0903 $\mu\text{mol/g/h}$, respectively, indicating that CO is the main product. Surprisingly, by photothermocatalysis, massive CO and CH_4 can be simultaneously produced. The production rates of CO and CH_4 are enhanced by 13.2 and 111.3 times, respectively. From the compared results between photocatalysis and photothermocatalysis, there is a photo-thermal synergy over sample AB-H-Co for catalytic reduction of CO_2 . The drastic enhancement of CH_4 production is mainly due to the grafting of ultra-small CoO_x rather than the introduction of oxygen vacancy, which will be discussed in detail later. TOF value is calculated to be 0.4936 h^{-1} according to the number of active sites of CoO_x . Assuming that CO and CH_4 are the only products in photothermocatalysis, the apparent quantum efficiency at 365 nm is $1.26 \times 10^{-2} \%$.

In the catalytic reduction of CO_2 , CO and CH_4 are produced via the transfer of two and eight electrons, as shown in the following equation:



The catalytic activity can be quantitatively evaluated by N-electrons, which is calculated according to the following equation.

$$\text{N-electrons} = 2n(\text{CO}) + 8n(\text{CH}_4),$$

where the $n(\text{CO})$ and $n(\text{CH}_4)$ mean consumption rate of electrons for production of CO and CH_4 , respectively. The calculated values are listed in Table 1. Accordingly, sample AB-H-Co again gives a much higher value of N-electrons via photothermocatalysis than that by photocatalysis (681.8×10^{17} vs 19.4×10^{17}). This further confirms the photothermal synergy over sample AB-H-Co for the catalytic reduction of CO_2 .

As is well reported, H_2O oxidation by photo-induced hole proceeds via two steps [58,59]. Firstly, H_2O is oxidized by hole to produce H^+ ions and OH· radical. Secondly, H_2O is oxidized by OH· radicals and holes to produce O_2 and H^+ . We try to measure the amount of O_2 over sample AB-H-Co, but no oxygen is detected. Herein, the missing of oxygen may be due to following factors: (1) consumption of O_2 through the reaction with photogenerated electrons; (2) back reaction of O_2 with H^+ or H_2 and (3) the low sensitivity of TCD for detection of trace O_2 production.

3.4.1. The photothermal synergy in CO_2 reduction over pristine AB

Fig. 5a shows the results of photocatalytic and photothermocatalytic reduction of CO_2 over pristine AB. In our previous work and others' work, pure TiO_2 was found inert at producing CH_4 via photocatalytic reduction of CO_2 , due to the limited onset of coupled multielectron-

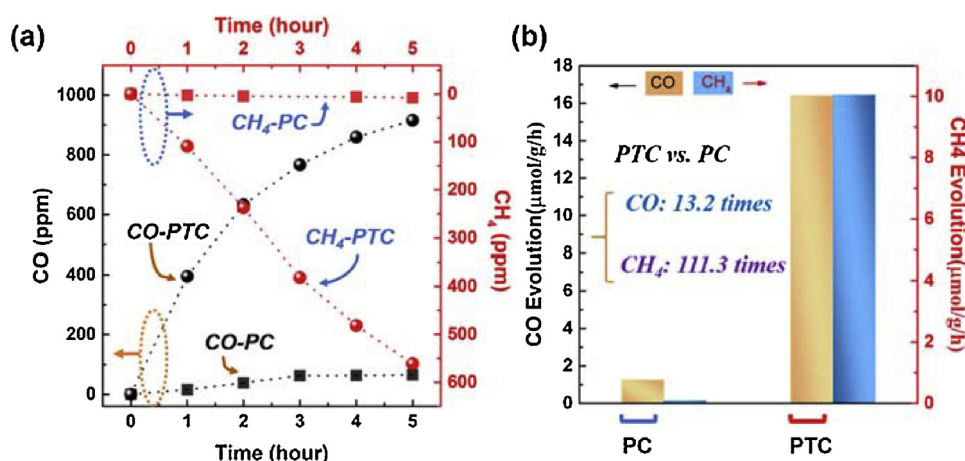


Fig. 4. (a) Time curves of CO and CH_4 production and (b) amount of CO and CH_4 formed in photocatalytic and photothermocatalytic CO_2 conversion over AB-H-Co. PC stands for photocatalysis and PTC stands for photothermocatalysis.

Table 1

Catalytic activities of photocatalytic and photothermocatalytic induced CO₂ conversion over different samples. a: Reaction conditions: room temperature, catalyst (0.05 g), $I_{365} = 20 \text{ mW cm}^{-2}$, 1.01 bar CO₂; b: Reaction conditions: $393 \pm 5 \text{ K}$, catalyst (0.05 g), $I_{365} = 20 \text{ mW cm}^{-2}$, 1.33 bar CO₂. c: CO-selectivity = $2 \times (\text{CO-yield}) / [2 \times (\text{CO-yield}) + 8(\text{CH}_4\text{-yield})]$; d: CH₄-selectivity = $8 \times \text{CH}_4\text{-yield} / [2 \times (\text{CO-yield}) + 8(\text{CH}_4\text{-yield})]$.

Sample	Photocatalysis ^a					Photothermocatalysis ^b				
	CO-yield (μmol/g/h)	CO-selectivity ^c	CH ₄ -yield (μmol/g/h)	CH ₄ -selectivity ^d	N-electrons (10 ¹⁷)	CO-yield (μmol/g/h)	CO-selectivity	CH ₄ -yield (μmol/g/h)	CH ₄ -selectivity	N-electrons (10 ¹⁷)
AB	0.6819	100%	/	/	8.2128	5.6656	96.11%	0.0574	3.89%	71.0018
AB-Co	0.9019	80.82%	0.0535	19.18%	13.4399	10.240	47.70%	2.8066	52.30%	258.5413
AB-Co-A	0.5786	83.98%	0.0276	16.02%	8.2983	8.7806	67.42%	1.0609	32.58%	156.8635
AB-H	0.4934	68.09%	0.0578	31.91%	8.7271	13.362	87.37%	0.4829	12.63%	184.1961
AB-Co-H	0.8105	81.50%	0.0460	18.50%	11.978	11.021	88.33%	0.3640	11.67%	150.2730
AB-H-Co	1.2473	77.54%	0.0903	22.46%	19.4017	16.403	28.98%	10.051	71.02%	681.7747

multiproton transfer ($8\text{e}^-/8\text{H}^+$) [60]. Thus, no CH₄ is likewise produced, and the apparent quantum efficiency at 365 nm is as low as $4.02 \times 10^{-4} \%$. In photothermocatalysis, very little CH₄ (0.05 μmol/g/h) is produced. However, there is a significant enhancement is observed in photothermocatalysis versus photocatalysis with regard to the production of CO. The CO production rate via photothermocatalysis is ca. 8.3 times higher than that of photocatalysis. Therefore, there is a photothermal synergy for enhanced production of CO versus CH₄.

3.4.2. The effect of the oxygen vacancies on the photothermal CO₂ reduction

To evaluate the influence of oxygen vacancy on photothermocatalytic reduction of CO₂, the catalytic activity of AB-H was tested and compared with AB. By photocatalysis, the AB-H is different from AB in that AB-H enables not only evolution of CO but also CH₄ from CO₂ reduction, as seen in Fig. 5b. Despite this, the activity

enhancement induced by oxygen vacancy via single photocatalysis is not striking. By photothermocatalysis, AB-H displays a more significantly enhanced production of CO and CH₄. The production rate of CO and CH₄ over AB-H is 27 and 8-fold higher than that via photocatalysis. Therefore, it can be concluded that photothermocatalysis is more promising than photocatalysis in CO₂ reduction, even introduction of a slight oxygen vacancy indeed results in a significantly enhanced production of CO and CH₄.

3.4.3. The effect of CoO_x and its dispersion on the photothermal CO₂ reduction

Fig. 5c shows the results of photocatalytic and photothermocatalytic reduction of CO₂ over AB-Co. By photocatalysis, the grafting of CoO_x leads to no obvious enhancement of CO and CH₄ production, which is limited by the ultra-low amount of CoO_x nanoparticles. However, by photothermocatalysis, impressive yields of products are observed. For

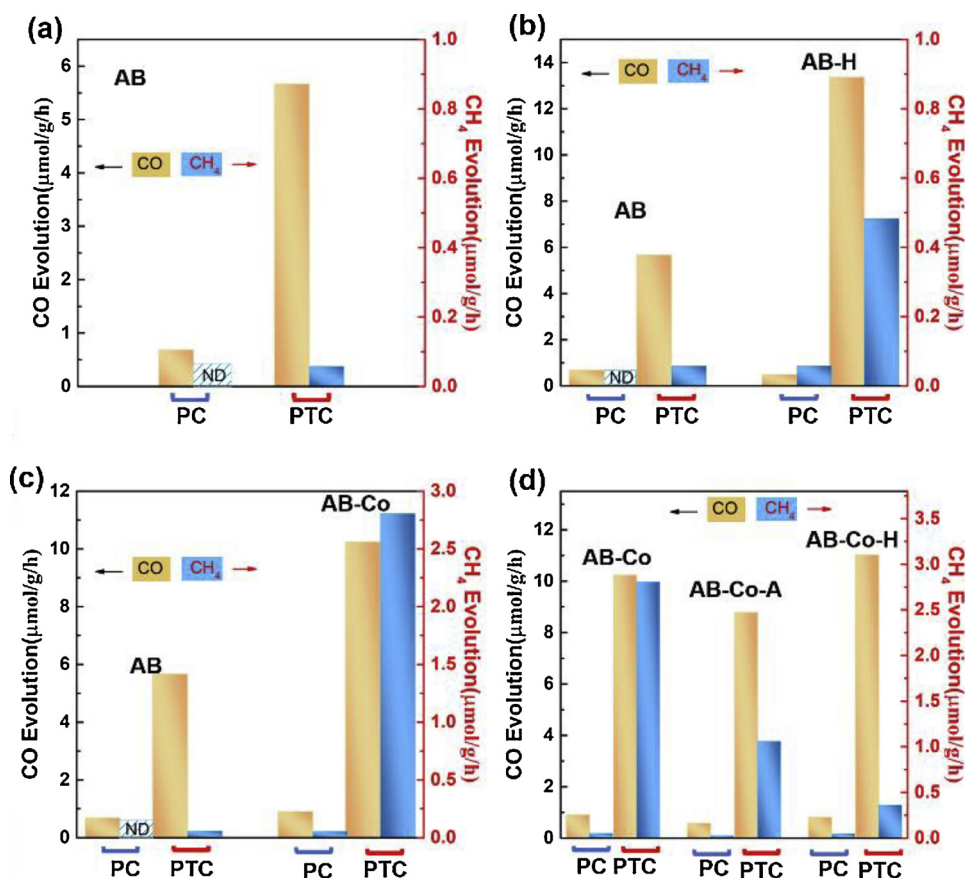


Fig. 5. Amount of CO and CH₄ formed in photocatalytic and photothermocatalytic induced CO₂ conversion over (a) AB; (b) AB and AB-H; (c) AB and AB-Co; and (d) AB-Co, AB-Co-A, and AB-Co-H. PC stands for photocatalysis and PTC stands for photothermocatalysis. ND = not detected.

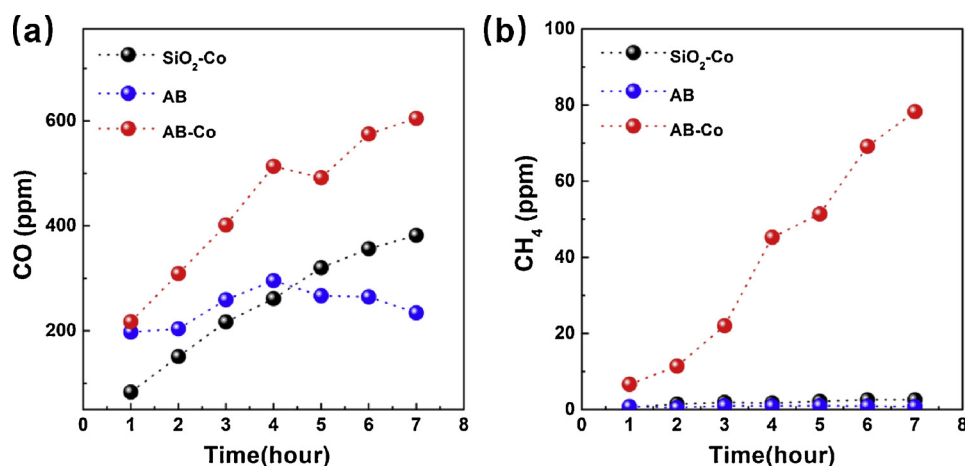


Fig. 6. Time curves of (a) CO and (b) CH₄ evolution in photothermocatalytic induced CO₂ conversion over AB, SiO₂-Co, and AB-Co.

CO production, the production rate over AB-Co is 11.35 times higher than AB and comparable to AB-H. For CH₄ production, the production rate over AB-Co is drastically increased by 52.46 times and far higher than that of AB and AB-H.

To verify the importance of photocatalyst support for CoO_x cocatalyst, a SiO₂/CoO_x catalyst was prepared under the same conditions as AB-Co. The preparation procedure is described in supporting information. The photothermocatalytic activity of SiO₂/CoO_x was tested and compared with AB-Co. As can be seen in Fig. 6, the CH₄ yield over AB-Co is far higher than SiO₂/CoO_x, indicating the irreplaceable role of TiO₂ support. Therefore, a synergy clearly exists between photocatalysis and thermocatalysis over AB-Co in CO₂ reduction, especially for the CH₄ production. The synergy solely benefits from CoO_x grafting, indicating that the CoO_x cocatalyst is a promising candidate to promote photothermocatalytic reduction of CO₂.

To further evaluate the effect of CoO_x dispersion on AB nanotubes, AB-Co sample was calcinated in air or N₂/H₂. Fig. 5d shows that calcination generally results in decreased activity over AB-Co. In detail, calcination in air leads to a simultaneously decreased production rate of CO and CH₄, and whereas calcination in N₂/H₂ selectively decreases the production rate of CH₄. Note that the calcination of AB-Co affects the production of CH₄ more significantly than that of CO. Upon calcination, CoO_x nanoparticles dispersed on AB nanotubes are believed to tend to aggregate and be of larger size, which is observed in HRTEM image in Fig. 1g and h. Therefore, it can be deduced that the high dispersion of CoO_x nanoparticles is essential in promoting photothermocatalytic reduction of CO₂. The higher dispersion of grafted CoO_x cocatalyst, the higher yield of CH₄ products.

3.4.4. The synergistic effect of oxygen vacancy and CoO_x on photothermocatalytic reduction of CO₂

As confirmed in aforementioned results, the introduced oxygen vacancy on AB nanotubes helps further dispersion of grafted CoO_x. When the loading is held constant among all the CoO_x grafted samples, the highest dispersion of CoO_x in AB-H-Co results in the smallest size of CoO_x. The size of CoO_x is too small to be observed by HRTEM, suggesting that CoO_x is monodispersed or even single-atom dispersed on the surface of the AB nanotubes. Fig. 7a and Table 1 compare the activities and selectivity of the photocatalytic and photothermocatalytic reduction of CO₂ over all samples. Sample AB-H-Co displays the champion value in the evolution of both CO and CH₄ products. The production rate of CH₄ is even 3.1 times higher than the sum of AB-H and AB-Co, confirming that an obvious synergy exists between the oxygen vacancy and the CoO_x cocatalyst. This synergy leads to an optimal dispersion of CoO_x cocatalyst and small size of CoO_x clusters. This leads to the highest photothermocatalytic activity of AB-H-Co. The

selectivity shows that oxygen vacancies help increase selectivity of CO and whereas CoO_x helps increase selectivity of CH₄ in PTC test. When the CoO_x and oxygen vacancies co-exist on the surface of AB nanotube, the synergistic effect between CoO_x and oxygen vacancies leads to the highest selectivity of CH₄, which is in consistence with its best PTC activity.

To evaluate the efficiency of the catalytic system, P25 and P25/CoO_x catalyst were prepared under the same conditions as AB-H-Co. The preparation procedure is described in supporting information. As shown in Fig. 7b, for PC, all three samples produce a slight amount of CO (ca. 1 μmol/g/h). Similar to AB-H-Co, CoO_x grafting on P25 leads to insignificant enhancement of photocatalytic activity. However, for PTC, the production rate of CH₄ over AB-H-Co is 8.82 and 3.16 times higher than reference samples of P25 and P25/CoO_x, respectively. Meanwhile, sample AB-H-Co displays comparable or even higher activity than that in other works (see Table S1), indicating the as-adopted PTC strategy is promising for CO₂ reduction.

In combination with above results of photothermocatalytic test over six typical samples, several conclusions can be drawn as follows:

- (1) By photocatalysis, AB enables CO₂ reduction to CO rather than CH₄. By photothermocatalysis, the catalytic activity can be greatly enhanced, but still limited to enhanced CO production.
- (2) By photocatalysis, neither the introduction of slight oxygen vacancies nor loading ultra-low amounts of CoO_x cocatalyst enhance the activity of CO₂ reduction. By photothermocatalysis, both approaches offer enhancement. Oxygen vacancy only promotes CO production whereas CoO_x cocatalyst promotes both CO and CH₄ production.
- (3) By photocatalysis, the synergy between oxygen vacancy and CoO_x cocatalyst leads to no activity enhancement. By photothermocatalysis, this synergy drastically promotes the reduction of CO₂, especially CH₄ production, benefiting from the optimal dispersion and smallest size of CoO_x cocatalyst.

3.5. Mechanism for the boosted activity of CO₂ reduction over photothermocatalyst

It is essential to first study the role of oxygen vacancy and CoO_x to understand the photothermocatalytic process of CO₂ reduction. Most research has focused on boosting CO₂ reduction via the introduction of oxygen vacancy. On one hand, the oxygen vacancy can decrease the adsorption and activation energy of CO₂. For example, STM studies have shown that CO₂ preferentially adsorbs on oxygen vacancy sites of TiO₂. The energy barrier for CO₂ hopping into an oxygen vacancy is 0.09 eV, which is much lower than 0.16 eV for CO₂ hopping out an

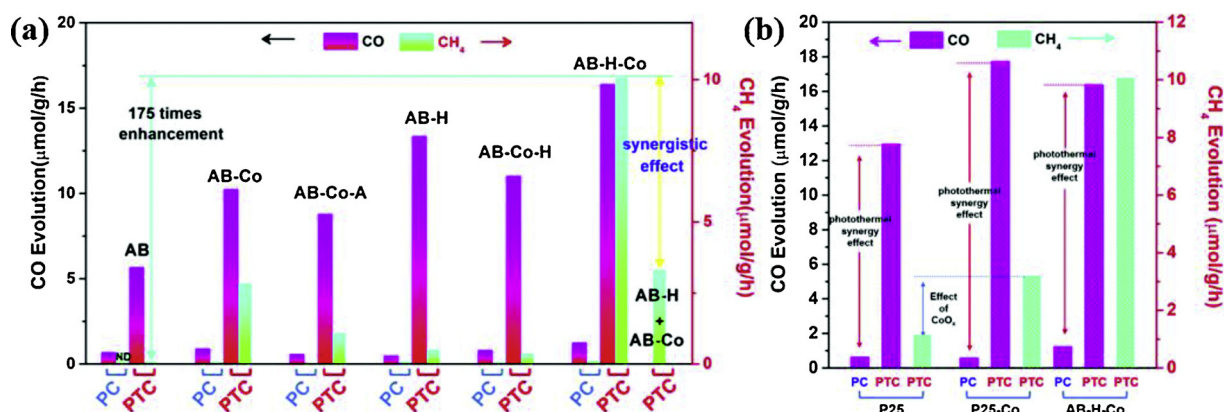


Fig. 7. a: Photocatalytic and photothermocatalytic induced CO_2 conversion over different samples; b: Histograms of catalytic production of CO and CH_4 over P25, P25-Co and AB-H-Co. PC stands for photocatalysis and PTC stands for photothermocatalysis. ND = not detected.

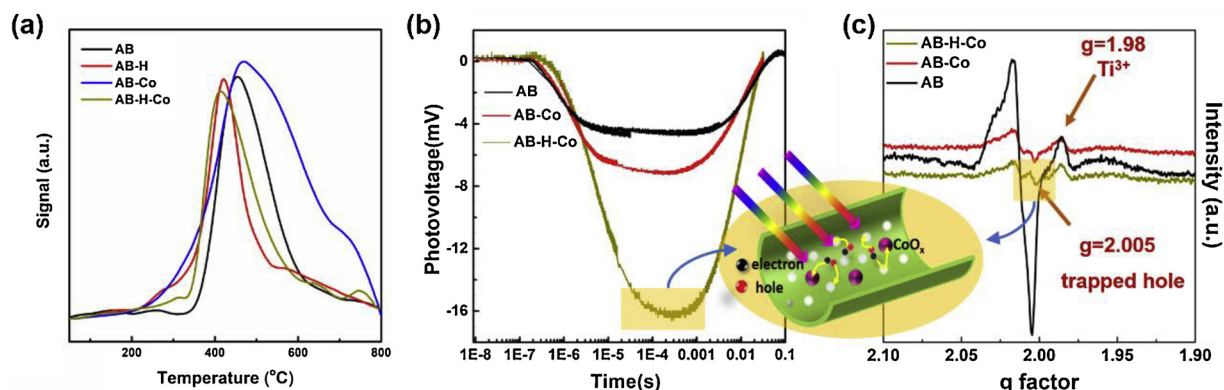


Fig. 8. (a): O_2 -TPD profiles of AB, AB-H, AB-Co, and AB-H-Co; (b): Transient photovoltage responses of AB, AB-Co, and AB-H-Co. The wavelength and the intensity of the laser are 355 nm and 100 μJ , respectively; (c): ESR spectra of AB, AB-Co, and AB-H-Co at 110 K with UV irradiation; inset shows a hole transfer over AB-H-Co.

oxygen vacancy [61]. The electron donating activity is increased nearby oxygen vacancies. At the oxygen vacancy defect, the initial step of CO_2 reduction can proceed and transient CO_2^- is formed via a one-electron transfer. Moreover, the barrier of two-electron reduction of CO at oxygen vacancies is 0.06 eV lower than the perfect TiO_2 [62,63]. On the other hand, the oxygen vacancy formed on the surface or sub-surface of TiO_2 is advantageous for electron trapping, which is beneficial for charge separation. In the point of thermocatalytic view, O_2 -TPD was performed to understand the role of oxygen vacancies. Fig. 8a shows that obvious oxygen desorption can be observed in the temperature range of 300–600 °C. As reported in the literatures, the desorption peaks in this range originate from desorption of subsurface lattice oxygen [64]. The temperature at peak maximum follows the sequence of AB-H-Co \sim AB-H < AB < AB-Co. Accordingly, the introduction of oxygen vacancy helps activate the lattice oxygen, and CoO_x enhanced the adsorption of the catalysts to oxygen. In fact, tremendous researches on thermocatalytic conversion of CO_2 have witnessed that oxygen vacancies are essential for endowing catalyst excellent ability of coke resistance [65]. This ensures a chemical looping reduction of CO_2 and high catalytic activity during the whole process. In this work, the as-observed lower activation temperature of lattice oxygen in sample AB-H-Co may inhibit carbon deposition. Moreover, the photothermal synergy could further facilitate the proton coupled reduction of carbon intermediate. Taking consideration of well-reported and consistent results on the positive role of oxygen vacancy for CO_2 reduction from viewpoint of thermodynamics, we believe that the advantages of oxygen vacancy played in photocatalysis are also applicable in photothermocatalysis.

To understand the role of CoO_x cocatalyst in CO_2 reduction, transient photovoltage spectra is required (Fig. 8b). At the time scale of

10^{-8} to 10^{-7} s, the photovoltages remain positive over all the samples, which is inconsistent with the nature of an n-type semiconductor. From 10^{-7} to 10^{-4} s, the photovoltage gradually changes from positive to negative, and the peak-valley value of photovoltage varies from each other. The value for AB-H-Co is the most negative, followed by AB-Co, and then AB. As is previously reported, the photovoltage response at this stage mainly reflects competition between diffusion and recombination of photogenerated electrons and holes [60,66,67]. During the diffusion process, there is a higher transfer rate of electrons, which usually leads to an accumulation of more electrons than holes, due to the lower effective mass of electron than a hole. Here, the consistent inverse of photovoltage response of all the samples agrees with this rule. Electron diffusion is accompanied by recombination with holes. When the recombination is inhibited by hole trapping, then the photovoltage is more negative and lasts for a longer time. In terms of the different responses of AB, AB-Co, and AB-H-Co, it is inferred that grafted CoO_x acts as a hole trap. Moreover, grafted CoO_x on AB-H works better for charge separation than that on AB. This inhibition of charge recombination by trapping holes around the surface CoO_x is conducive not only to the accumulation of electrons for multi-electron transfer but also oxidation of water for multi-proton release. Thus, the photothermocatalytic activity enhanced by CoO_x catalyst is closely correlated with its role in hole transfer from AB nanotube.

To further evident the effect of hole trapping by CoO_x , ESR spectra were collected over AB, AB-H, AB-Co, AB-H-Co and shown in Fig. 8c. In general, the ESR signals over irradiated TiO_2 at a lower temperature (< 150 K) display two features. One feature is located at $g_{\perp} = 1.99$ –1.97, which is assigned to trapped electrons in terms of Ti^{3+} . The other feature is located at $g = 2.002$ –2.030, which is assigned to trapped holes and superimposed oxygen species of O^- and O_2^- . For

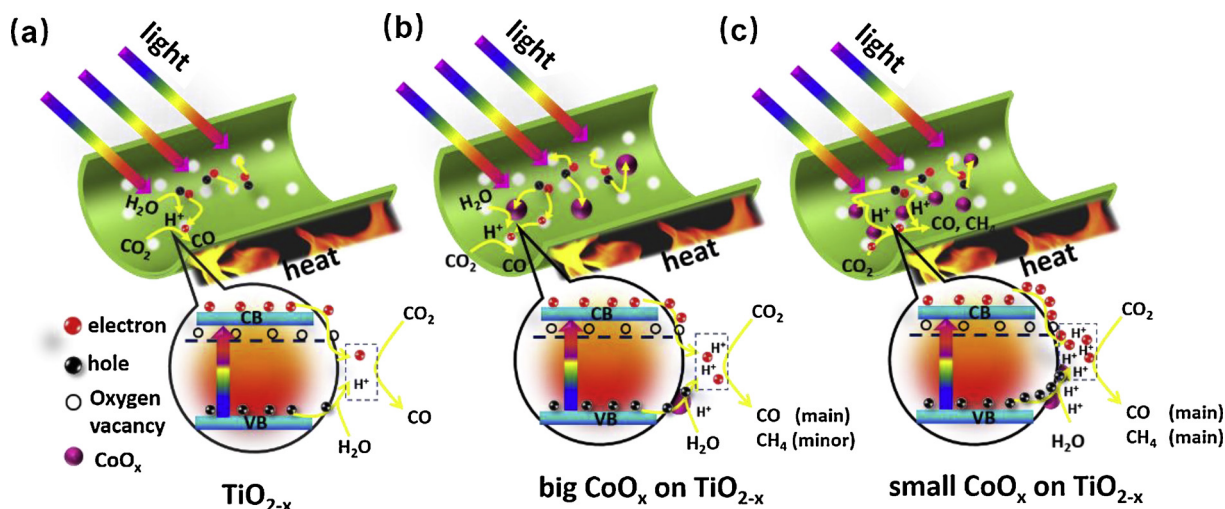


Fig. 9. Scheme of photothermocatalytic reaction over three typical samples: (a): TiO_{2-x} ; (b): big CoO_x clusters modified TiO_{2-x} ; and (c): small CoO_x clusters modified TiO_{2-x} .

sample AB, strong signals can be observed in the region of $g = 2.00$ – 2.03 . After CoO_x grafting, there is no obvious decrease in signal intensity at $g = 1.99$, indicating that grafting of CoO_x could not interrupt the trapping of photogenerated electrons. Conversely, the initially strong signals over AB obviously decrease after CoO_x grafting, which can be observed in both AB-Co and AB-H-Co. Since the trapping of electrons is not interrupted, the decrease in signals is mainly related to the inhibition of O^- species. As is well documented, the O^- species are formed via the reaction of holes with surface bridging oxygen atoms or lattice oxygen atoms, hence the decrease of the signal of O^- species means decreased holes on TiO_2 . This decrease of holes suggests a transfer of holes from TiO_2 to CoO_x . Meanwhile, on a closer inspection of spectra in the region of $g = 2.00$ – 2.03 , an additional signal appears at $g = 2.005$. As demonstrated by Nosaka and others, trapped holes give the characteristic signal at $g = 2.005$ [68]. Thus, the additional signal at $g = 2.005$ likely results from the trapped holes due to the presence of a CoO_x site. In combination with the decreased signal of O^- species around TiO_2 and trapped holes, we conclude that grafting of CoO_x plays an important role in extracting holes from TiO_2 .

Fig. 9 illustrates the mechanism of photothermocatalytic reduction of CO_2 over the $\text{TiO}_{2-x}/\text{CoO}_x$. CO_2 is initially adsorbed by the oxygen vacancy on the surface of the nanotube. Upon excitation by UV light, the photogenerated electrons tend to be trapped by oxygen vacancies and transfer to adsorbed CO_2 , as shown in Fig. 9a. Meanwhile, the photogenerated holes tend to be trapped by surface CoO_x cocatalysts. Oxidation of H_2O proceeds at CoO_x site and the proton is released, as shown in Fig. 9b. To access CO_2 reduction, electron transfer and proton transfer is expected to be synchronous. Since the time scale for electron transfer and proton transfer stays on picosecond and hundreds of microseconds, the rate determining step is proton transfer process. The imposed thermal radiation leads to enhanced proton transfer. This benefits multiple proton/electron coupling. Moreover, in comparison with other CoO_x modified AB samples, the smaller size of CoO_x allows quicker transfer of trapped holes to H_2O , producing more protons for CO_2 reduction, as shown in Fig. 9c. Therefore, the photothermocatalytic activity is superior to other AB samples modified by larger sized CoO_x .

4. Conclusion

In summary, we have developed an efficient photothermocatalyst by modifying TiO_2 nanotube with slight oxygen vacancies and ultralow amount of CoO_x . Its photothermocatalytic activity in terms of CH_4 evolution is 111 times higher than single photocatalysis and 175 times higher than that of pristine TiO_2 . Comprehensive analysis reveals that

the introduction of oxygen vacancies is beneficial for the charge separation and dispersion of CoO_x cocatalyst, and the grafted CoO_x acts as a hole trap and promotes the release of more protons. Thus, there is more opportunity for provided for CH_4 production after grafting CoO_x cocatalyst around the oxygen vacancies. This work presents a different insight by comparing photothermocatalysis and photocatalysis. It offers a novel route for the design of highly efficient photothermocatalysts towards CO_2 reduction.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.11.022>.

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